Toughened Carbon Fiber Fabric-Reinforced pCBT Composites

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Toughened carbon fiber-fabric reinforced polymerized cyclic butylene terephthalate (pCBT) composites were obtained by chemical modification of cyclic butylene terephthalate (CBT) with small amounts of epoxy resin and isocyanates as chain extenders. Homogeneous CBT/epoxy and CBT/isocyanate blends were prepared by melt blending the components in a lab-scale batch mixer at low temperatures and high shear rate. Melt blending was stopped before the ring-opening polymerization of CBT could start. The modified CBT was the starting material for carbon fiber fabric-reinforced pCBT composites (fiber content at about 65 wt%) which were prepared by ring-opening polymerization during compression molding using a simple powder prepreg method. Interlaminar shear strength, flexural strength, and failure strain of the chemically modified composites increased up to 60% with respect to unmodified pCBT composites. Nevertheless, the flexural moduli slightly decreased due to the toughening effect of the chain extender on the pCBT matrix. Drop weight impact tests revealed that the energy absorption of the modified composites was relatively higher as compared to unmodified pCBT composites. POLYM. COMPOS., 00:000–000, 2014. © 2014 Society of Plastics Engineers

INTRODUCTION

The interest in thermoplastic composites (TPCs) has increased in the past years because TPCs typically outperform thermosets in toughness and impact strength. Moreover, TPCs can be produced in a shorter time as compared to thermosets because no curing step is needed. Additionally, they can be welded and recycled due to their meltability. However, the main disadvantage of thermoplastics is the need for high processing temperatures and pressures due to the high melt viscosity of the matrix. In addition, proper impregnation of the fiber at a micro level might prove difficult and often results in products with a locally high void content [1].

These shortcomings can be overcome using ring-opening polymerization (ROP) of cyclic oligomers such as cyclic butylene terephthalate oligomers (CBT®) which exhibit a very low, water-like melt viscosity (0.02 Pa s at 190°C [2]). CBT oligomers undergo an entropically driven ROP in the presence of a tin-based catalyst at temperatures below as well as above the melting temperature (T_m) of polymerized CBT (referred to as pCBT), i.e., $T_m = 225°C$ [3]. This allows for isothermal processing below T_m where crystallization and polymerization occur simultaneously, hence demolding can be done without further cooling [4–6].

Nevertheless, pCBT was shown to be considerably more brittle than conventional PBT [5, 7]. The pCBT brittleness is due to a relatively higher degree of crystallinity together with the formation of large perfect crystals and a lack of intercrystalline tie molecules [5, 8]. The inherent brittleness of pCBT is a critical problem and complicates a wide application of fiber reinforced pCBT composites as structural materials and at industrial scales. This problem has been addressed by various researchers, e.g., by decreasing the crystallinity and thus increasing the toughness, either by nonisothermal processing using fast cooling [9] or copolymerization of CBT with poly(-ethylene-*co*-vinyl acetate) [10], poly(vinyl butyral) [11], ε-caprolactone [12], and polycaprolactone [13]. However, these methods are little effective or lead to a decrease of other relevant mechanical properties, such as stiffness and strength. Wu et al. [14–16] proposed a toughening concept for textile reinforced pCBT composites by applying an epoxy preforming binder among textile fabric layers. The pCBT matrix in the interply region was toughened. Nevertheless, the brittle nature inherent in the composite

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laminate based on pCBT matrix was not completely eliminated with the proposed concept. This was because the pCBT polymer matrix was toughened locally since the preforming binder was mainly located in the interply region of the composite laminate whereas bulk pCBT remained brittle.

Recently, we showed that reactive chain extension of pCBT with epoxy resin [17] as well as isocyanates [18] is a useful way to increase the molecular weight and to toughen pCBT without considerably affecting other properties. In this work, it is demonstrated that the developed toughening methods not only work for pCBT matrix but also for fiber reinforced pCBT composites.

EXPERIMENTAL SECTION

Materials

Cyclic butylene terephthalate oligomers were termed as one-component CBT®160 and contained butyl tin chloride dihydroxide as a catalyst. The material was provided as granules by Cyclics Europe GmbH (Schwarzheide, Germany). A low-viscous, bifunctional epoxy resin (referred to as EP), Eporai 450/A was purchased from IQRaisa, S.L. (Valencia, Spain). The epoxy equivalent weight was 148–155 g/eq.

Three different types of isocyanates were used as toughening agents; a bifunctional liquid aliphatic hexamethylene diisocyanate (referred to as HDI) with a molecular weight of 168.2 g/mol, a bifunctional solid aromatic 4,4″-methylenebis(phenyl isocyanate) (referred to as MDI) with a molecular weight of 250.3 g/mol and a solid polymeric methylene diphenyl diisocyanate (referred to as PMDI). The PMDI was based on 4,4″-methylenebis(phenyl isocyanate) and contained oligomers with an average functionality of ~2.7 and an NCO content of 31.8%. HDI and MDI were obtained from Sigma-Aldrich (St. Louis, MO, USA) while PMDI was purchased from BASF Poliuretanos Iberia SA (Rubí, Spain). All toughening agents were used as received.

The reinforcement used in the pCBT composites was a high strength carbon fiber fabric with balanced plain weave architecture, referred to as CF. It consisted of two sets of interlacing threads, commonly referred to as warp and weft, and was a bidirectional [0/90]. It was characterized by a surface weight of 193 g/m^2 and was supplied by Jordi Sagristà, SL (Barcelona, Spain) with the reference TAFE 3K.

Sample Preparation

The CBT was ground into a fine powder using mortar and pestle and vacuum dried at 80°C for 8 h prior to processing. EP- and NCO-modified CBT as starting materials for composite production were prepared by melt blending in a lab-scale batch mixer (Brabender Plasti-Corder W50EHT, Brabender GmbH & Co. KG, Duisburg, Germany). This step is necessary, also for large scale production (i.e., compression molding or resin transfer molding), because dry blending of the components did not yield homogeneous CBT/chain extender blends. CBT and toughening agent were melt blended in the batch mixer for a short time; the difficulty was to operate the batch mixer in such a manner, that good melt homogeneity was achieved without prematurely polymerizing the CBT. Preliminary studies were performed to determine the optimum processing parameters. A mixing chamber temperature of 200°C, rotor speed of 180 min^{-1} and under a blanket of nitrogen for 2 min appeared optimum. These processing parameters were used for all CBT/toughening agent blends. Proof that the prepared blends did not polymerize prematurely during melt blending is shown in Fig. 1. Here, unmodified CBT, CBT/EP 3%, and CBT/PMDI 1% dry blends are exemplarily shown to demonstrate that ROP did not start during the first 2 min of mixing. The dashed vertical line indicates the end of the melt blending process after 2 min. It can be seen that the torque was 0 ± 0.1 Nm during this period; hence, the CBT blends were molten and exhibited their typical water-like viscosity prior to ROP. Longer mixing times resulted in a steep torque increase, i.e., the onset of polymerization.

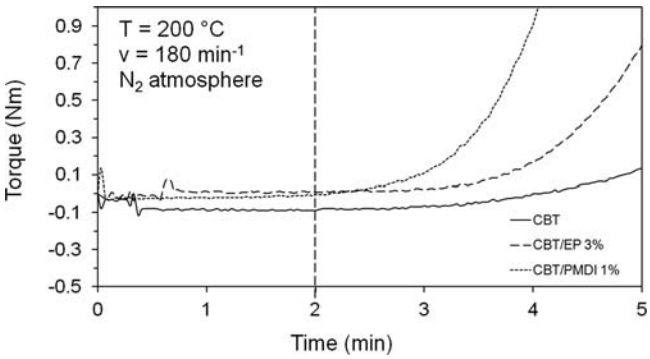

FIG. 1. Representative torque curves of pristine and modified CBT premixes.

Fresh CBT/modifier blends were prepared as follows. Around 40 g of previously dried CBT and the corresponding amount of chain extender were melt blended for 2 min. Then the liquid materials were quickly collected from the mixing chamber (they readily flowed out of the mixing chamber due to their low viscosity), cooled to room temperature (RT), ground into a fine powder using mortar and pestle, vacuum dried for 8 h at 80°C, and subsequently used to prepare the modified pCBT-CF composites. Premixes containing 2, 3, and 4 wt% of EP as well as blends containing 1 wt% of PMDI, MDI, and HDI, respectively, were prepared.

A simple powder prepreg method was used to manufacture pCBT-CF composites via compression molding. The composite lay-up was as follows. Previously dried CBT/chain extender powder (~1.1 g) was evenly spread on a CF fabric (size: 10 × 10 cm^2; weight: ~2 g; vacuum

TABLE 1. Polymer and composite densities, fiber weight fractions, and void contents of unmodified and modified pCBT-CF composites.

Sample	Polymer density (g/cm^3)	Composite density (g/cm^3)	Fiber weight fraction (wt%)	Void Content (%)
pCBT-CF	1.33	1.58	66.5 ± 1.4	0.8
pCBT/EP 2%-CF	1.33	1.58	58.5 ± 6.6	0.5
pCBT/EP 3%-CF	1.33	1.59	66.8 ± 2.3	0.6
pCBT/EP 4%-CF	1.33	1.57	64.0 ± 2.5	1.1
pCBT/PMDI 1%-CF	1.32	1.59	70.5 ± 3.1	1.5
pCBT/MDI 1%-CF	1.33	1.58	66.1 ± 3.1	1.0
pCBT/HDI 1%-CF	1.32	1.59	67.6 ± 0.3	1.0

dried for 8 h at 80°C). In this manner, two types of powder prepregs consisting of 10 or 20 layers of CF fabric and 9 or 19 layers of CBT powder, respectively, were prepared. The related composites were designated as $[0/90]_{10}$ and $[0/90]_{20}$, respectively. The powder prepregs were placed between two PTFE-covered steel plates and compression molded at 230°C in an IQAP LAP PL-15 hot plate press (IQAP SL, Barcelona, Spain). A pressure of 0.5 MPa was applied for 10 s in order to compact the powder prepreg and to facilitate melting. Then the pressure was released, i.e., the moving hot plate remained in its position without applying pressure, and the powder prepreg was *in situ* polymerized. During the last 2 min of the polymerization step a pressure of 3 MPa was applied in order to compact the composite. Then the sample was cooled at ca. −50°C/min to RT under the same pressure. The polymerization time was 20 min for pristine CBT samples as well as for samples containing EP. Isocyanate-modified samples were polymerized for 15 min because of the fast chain extension reaction of the CBT/isocyanate blend [18]. $[0/90]_{10}$ composites had a nominal thickness of 1.5 mm and were used for microscopy, dynamic mechanical thermal analysis (DMTA), and mechanical testing. $[0/90]_{20}$ composites had a nominal thickness of 3 mm and were used for puncture impact properties determination. All specimens were obtained by water jet cutting.

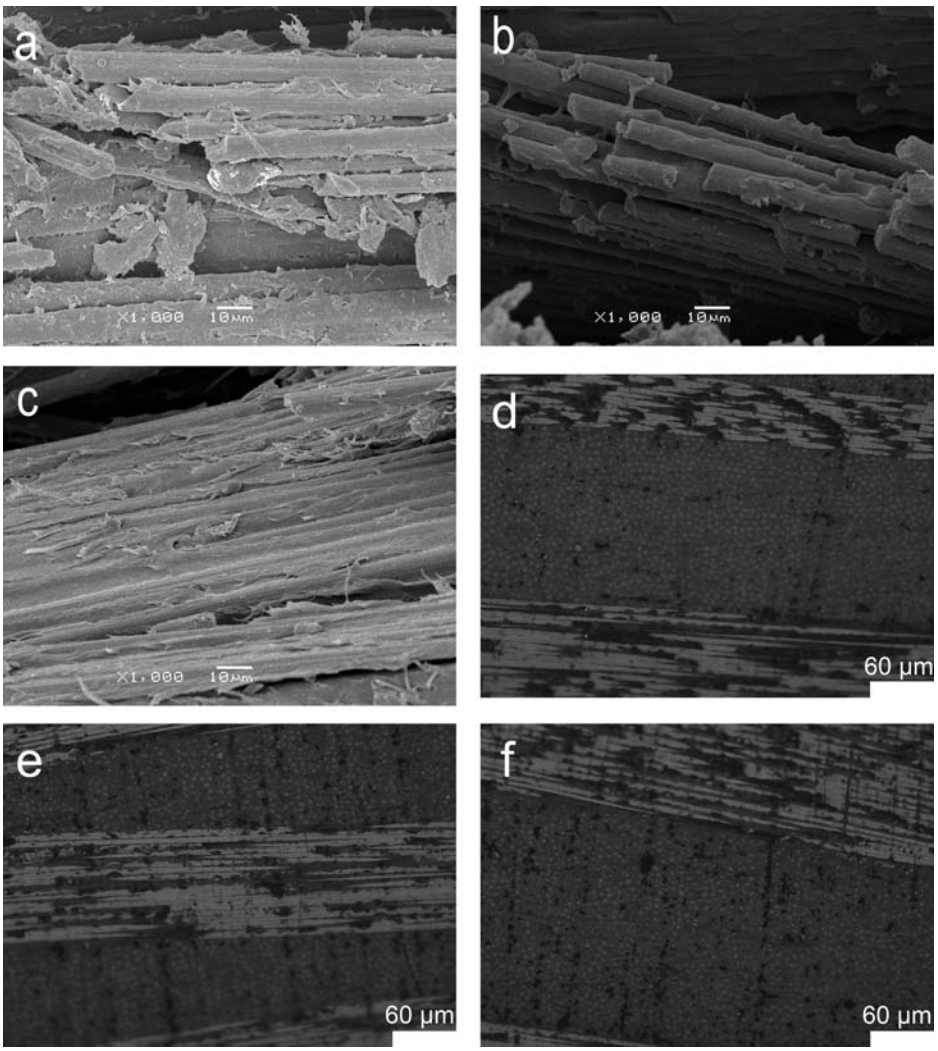

FIG. 2. SEM morphologies of fracture surfaces of cryofractured samples of pCBT-CF (a), pCBT/EP 3%-CF (b), and pCBT/PMDI 1%-CF (c); pictures were taken normal to fiber direction. OM micrographs of polished surfaces of pCBT-CF (d), pCBT/EP 3%-CF (e), and pCBT/PMDI 1%-CF (f).

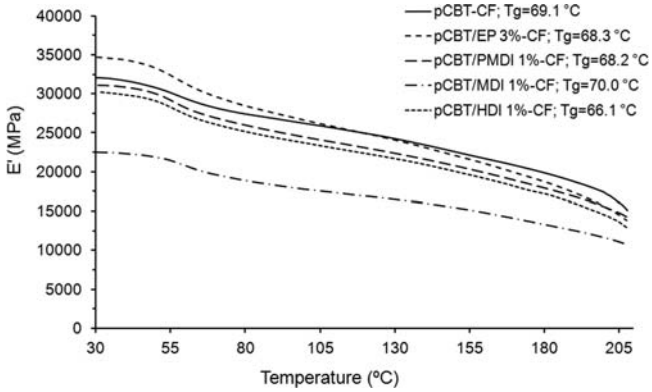

FIG. 3. DMTA storage modulus curves of pristine, epoxy-modified, and isocyanate-modified pCBT composites.

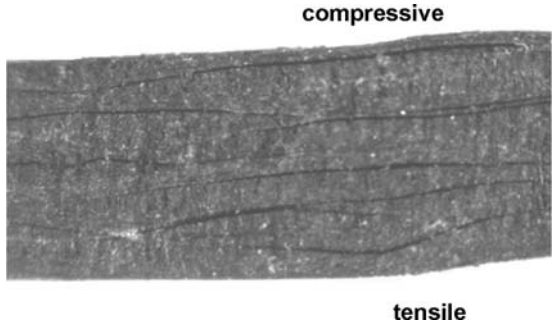

FIG. 4. Lateral view of a pCBT-CF composite sample exhibiting multiple interlaminar shear failures after short beam interlaminar shear strength testing. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.] AQ2

Characterization

Unmodified and modified pCBT-CF composites were characterized by DMTA using a Q800 TA device (TA Instruments, New Castle, DE) in single cantilever mode at a frequency of 1 Hz and a strain of 0.01%. The temperature range was set from 30 to 210°C at a heating rate of 2°C/min and the composite sheets had dimensions of ca. 20 × 15 × 1.5 mm^3. The span length was set to 17 mm for all experiments. The density of the pCBT-CF composites was determined according to ISO 1183 method A. Fiber weight contents of the pCBT-CF composites were determined by direct calcination in a Q600 device (TA Instruments, New Castle, DE) using dry nitrogen. Samples with a weight of 20–30 mg were heated in aluminum oxide pans from RT to 600°C at a heating rate of 10°C/min and then isothermally hold for 3 h. The void content of pCBT-CF composites was calculated according to ISO 7822 method A. The morphology was analyzed by scanning electron microscopy (SEM) on fracture surfaces of cryo-fractured composite samples using a Jeol JSM-5610 microscope (Jeol, Tokyo, Japan) using an acceleration voltage of 10 kV. The fracture surfaces were sputter coated with a thin gold layer using a Bal-Tec SCD005 Sputter Coater (Bal-Tec, Liechtenstein). Optical microscopy (OM) was used to study the fiber distribution and impregnation on polished pCBT composites (Leica MEF4, Leica Microsystems GmbH, Wetzlar, Germany).

TABLE 2. Flexural properties and apparent interlaminar shear strengths of unmodified and modified pCBT-CF composites.

Sample	Flexural modulus (GPa)	Flexural Strength (MPa)	Failure strain (%)	ILSS (MPa)
pCBT-CF	35.3 ± 7.0	453 ± 31	1.1 ± 0.1	29.6 ± 2.0
pCBT/EP 2%-CF	27.0 ± 3.8	692 ± 53	1.8 ± 0.2	45.2 ± 6.0
pCBT/EP 3%-CF	37.7 ± 5.5	736 ± 86	1.5 ± 0.2	40.8 ± 3.3
pCBT/EP 4%-CF	33.0 ± 5.5	703 ± 66	1.4 ± 0.2	40.1 ± 1.4
pCBT/PMDI 1%-CF	34.7 ± 6.8	668 ± 79	1.4 ± 0.2	42.2 ± 3.2
pCBT/MDI 1%-CF	34.3 ± 6.5	476 ± 29	1.2 ± 0.1	28.1 ± 3.6
pCBT/HDI 1%-CF	34.1 ± 5.9	680 ± 152	1.3 ± 0.3	42.5 ± 2.0

The flexural properties of pCBT-CF composites were determined according to ISO 14125 method A at RT on a Galdabini Sun 2500 universal testing machine (Galdabini, Cardano al Campo, Italy) using a crosshead speed of 1 mm/min. The specimens had dimensions of $l = 30$ mm, $b = 15$ mm, $h = 1.5$ mm, and the span L was 24 mm. The short beam interlaminar shear strength (ILSS) was determined according to ISO 14130 at RT and a crosshead speed of 1 mm/min was used on the above mentioned universal testing machine. Specimens had dimensions of $l = 15$ mm, $b = 7.5$ mm and a thickness of $h = 1.5$ mm. Drop weight impact properties were determined at RT according to ISO 6603-2. A Ceast Fractovis Plus (Ceast, Pianezza, Italy) instrumented drop weight impact testing machine was used. The hemispherical striker tip had a diameter of 20 mm and was lubricated prior to impact tests. $[0/90]_{20}$ composite specimens were placed simply supported on an annular ring with inner and outer diameter of 40 and 60 mm, respectively. The nominal impact energy (E_0) ranged from 0.5 to 20 J and the impact velocity (v_0) ranged from 0.5 to 3.3 m/s. Contact force–real time history was stored at a sampling rate of 333 kHz. Energy, velocity, and deflection were numerically deduced from the force–time data.

RESULTS AND DISCUSSION

Physical Properties

The density, fiber- and void contents of the prepared composites are compiled in Table 1. It can be seen that the T1 chemical modifications did not significantly alter the densities of the polymers and composites. The void contents of the composites were in the range of 0.5–1.5%, which are in good agreement with published results. Mohd Ishak et al. [7] reported void contents of <1 and 4.7% for pressure-controlled and for displacement-controlled conditions, respectively. Using vacuum infusion, Agirregomezkorta et al. [19] obtained a void content of 3.3%.

Void content was lower in epoxy-modified samples but apparently increased with the amount of EP, reaching the

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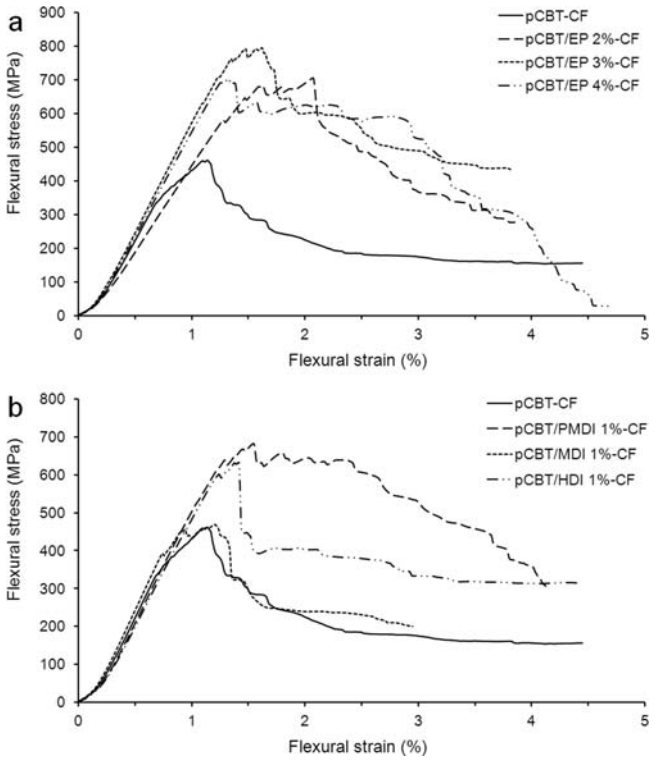

FIG. 5. Typical three-point-bending stress-strain curves for neat as well as (a) epoxy-modified and (b) isocyanate-modified pCBT-CF composites.

highest value of 1.1% when 4 wt% of EP was used. This may be ascribed to a hampered fiber impregnation due to the increasing viscosity of the CBT/EP blends with EP caused by the relatively higher viscosity of EP resin as compared to molten CBT. The isocyanate modification led to a void content of 1–1.5%, depending on the type of isocyanate used. Isocyanates preferably react with pCBT carboxylic end groups, thereby releasing CO_2 during amidation [20]. Therefore, the relatively higher void contents of isocyanate-modified samples can be attributed to the CO_2 release during chain extension. Nevertheless, the polymerization step during molding was pressure-less and the entrapped gas in the composite could escape, therefore a similar void content level was reached in all composites.

Morphology

The morphologies as well as fiber distribution and impregnation of pCBT-CF, pCBT/EP 3%-CF, and pCBT/PMDI 1%-CF were assessed by SEM analysis (c.f. Fig. F2 2a–c) and OM analysis (Fig. 2d–f). Generally, no significant differences between the prepared composites were observed. SEM morphologies show that some matrix material was bonded to the carbon fibers, indicating a good interfacial adhesion between fiber and matrix in all cases. Regarding the OM micrographs, warp, and weft rovings and a good macroimpregnation can be seen on a macroscopic scale. Taking a closer look, one can see a uniform interfiber distribution and a good microimpregnation in all composites. Good fiber impregnation is observed because the low viscosity of the molten CBT facilitates the penetration of the resin through the fabric and the impregnation of intra-bundle fibers [7, 19, 21]. Nevertheless, some intrabundle voids were detected which are in line with the calculated void contents of 0.5–1.5%.

DMTA Analysis

The stiffness as a function of temperature of the prepared composites was studied using DMTA; results are shown in Fig. 3. The observed DMTA storage moduli at F3 RT agree well with the flexural moduli as will be shown later. It can be seen that the highest stiffness at RT was found for the sample containing 3 wt% of EP. Then it decreased with temperature and reached a storage modulus equal to the one of neat pCBT-CF at 119°C. Storage moduli of isocyanate-modified composites were similar to the one of pristine pCBT-CF, but all curves ran below the one of the unmodified sample. An exception was the sample containing MDI which exhibited the lowest stiffness together with the highest T_g of all tested samples. As will be shown later, this sample also exhibited poor interlaminar shear strength as well as inferior flexural properties.

Short Beam Interlaminar Shear Strength

The apparent interlaminar shear strengths of unmodified and modified pCBT-CF composites were determined; results are listed in Table 2. All tested samples failed by T2 multiple interlaminar shear failures as exemplarily shown in Fig. 4, were cracks (visible as black lines) propagated F4 between the reinforcement layers in normal direction to the applied load. It can be seen that pCBT-CF exhibited a rather low interlaminar shear strength of 30 MPa due to its brittle behavior, which is in good agreement with values published in the literature [7, 19, 22]. Apparent interlaminar shear strength remarkably increased by 35–53% when the pCBT composites were toughened with EP and NCO; the highest observed *ILSS* was 45 MPa and was found for the sample containing 2 wt% of EP. Nevertheless, an exception was the sample containing MDI; its *ILSS* value decreased by 5% with respect to the unmodified sample. Recall from [18] that MDI showed only a minor toughening effect on pCBT as compared to PMDI, HDI and EP, respectively. This demonstrates that EP, PMDI, and HDI are effective toughening agents for fiber reinforced pCBT composites.

Flexural Properties

The flexural properties of unmodified and modified pCBT-CF composites were determined; results are shown in Fig. 5 as well as in Table 2. F5

The failure modes of unmodified and modified pCBT composites were tensile fracture at the outermost layer and compressive failure including interply fracture. The

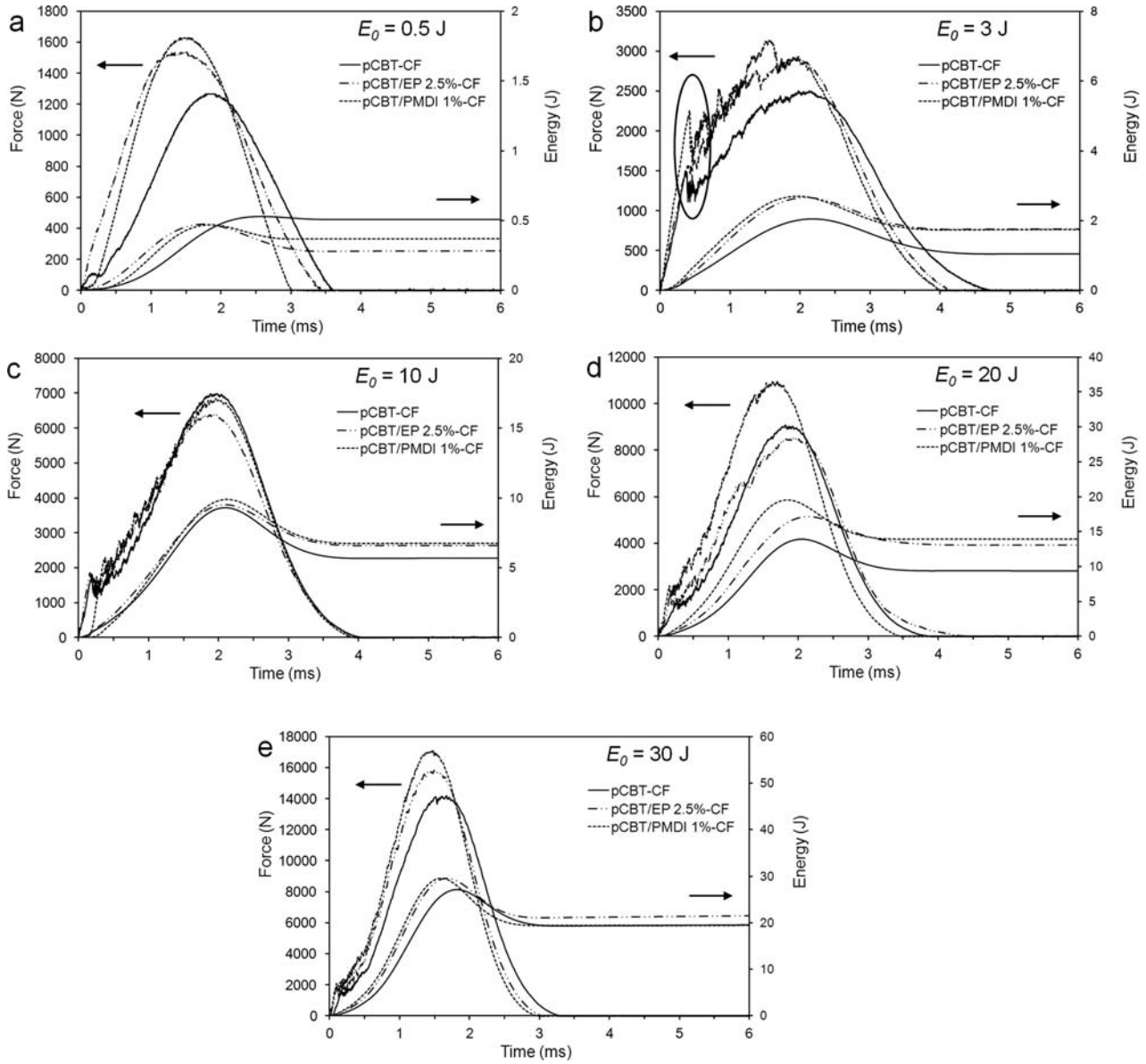

FIG. 6. Force and absorbed energy *versus* time plots of pCBT-CF, pCBT/EP 2.5%-CF and pCBT/PMDI 1%-CF composites; subcritical impact (a) and supercritical impacts (b–d).

brittleness and pronounced notch sensitivity of pCBT-CF is well reflected in the low flexural strength and failure strain (linked with the maximum stress), whereas the relatively high flexural modulus may be ascribed by the somewhat higher degree of crystallinity [17, 18]. Apparently, the maximum composite strength could not be reached because the matrix failed before the fiber reinforcement reached its maximum strength.

In contrast, all modified samples exhibited a much higher strength and failure strain but a slightly lower stiffness due to the toughening effect of the chain extenders. Flexural strength generally increased by ca. 50% and failure strain increased by up to 63% when the pCBT composites were toughened with EP and NCO. If failure strain is taken as a criterion for toughness, then the toughest sample was pCBT/EP 2%-CF whereas the stiffest and strongest sample was the one containing 3 wt% of EP. Again, an exception was the sample containing MDI; this sample showed only minor improvement in strength and toughness. These results are in line with the earlier discussed mechanical performances of the EP- and NCO-modified pCBT matrices [17, 18] and show that EP, PMDI, and HDI effectively toughen fiber reinforced pCBT composites.

Drop *Weight Impact Properties*

The drop weight impact properties of unmodified and modified pCBT-CF composites were determined; contact force–real-time curves are shown in Fig. 6 and F6

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TABLE 3. Drop weight impact properties of unmodified and modified pCBT-CF composites.

E_0 (J)	Sample	E_{crit} (J)	F_d (N)	F_M (N)	t_c (ms)	l_M (mm)	E_{abs} (J)
	pCBT-CF	–	–	1,264	3.6	0.8	0.4
0.5	pCBT/EP 2.5%-CF	–	–	1,535	3.4	0.5	0.5
	pCBT/PMDI 1%-CF	–	–	1,625	3.0	0.6	0.4
	pCBT-CF	0.3	1,490	2,501	4.7	1.4	2.0
3	pCBT/EP 2.5%-CF	0.4	1,562	2,926	4.1	1.5	2.6
	pCBT/PMDI 1%-CF	0.4	2,256	3,133	4.0	1.3	2.5
	pCBT-CF	0.3	1,643	6,998	4.0	3.1	9.2
10	pCBT/EP 2.5%-CF	0.3	1,860	6,384	4.0	3.0	9.4
	pCBT/PMDI 1%-CF	0.6	2,294	6,854	3.9	3.2	9.7
	pCBT-CF	0.4	1,517	9,066	3.9	3.8	13.3
20	pCBT/EP 2.5%-CF	0.6	1,806	8,533	4.4	4.2	16.9
	pCBT/PMDI 1%-CF	0.5	2,176	10,971	3.5	3.9	18.9
	pCBT-CF	0.3	1,598	14,177	3.3	4.8	26.5
30	pCBT/EP 2.5%-CF	0.3	1,860	15,839	3.0	4.6	28.6
	pCBT/PMDI 1%-CF	0.4	2,068	17,121	3.0	4.4	29.0

m_{impact}: 3.62 kg; h_{impact}: 13–563 mm; v_{impact}: 0.5–3.3 m/s.

T3 impact data is presented in Table 3. For the sake of clarity, only one $[0/90]_{20}$ composite for each group of chain extenders with the best mechanical performance was prepared and impact tested as described above; namely, pCBT-CF, pCBT/EP 2.5%-CF, and pCBT/PMDI 1%-CF.

Impact events can be divided into subcritical impacts with no damage and supercritical impacts with delamination. The impact energy at which the first damage occurs is referred to as the delamination threshold energy or also as the critical energy, E_{crit}. The corresponding delamination threshold force, F_d, is defined as the point at which a significant drop in contact force occurs [exemplarily marked by an ellipse in Fig. 6b. It was shown that this delamination threshold force does not depend on the nominal impact energy, E_0 [23]. The maximum contact force during impact is called the peak force, F_M. The difference between maximum energy, E_M, and absorbed energy, E_{abs}, is the rebound energy or elastic energy. Total contact time is referred to as t_c and deflection at the peak force is denoted as l_M.

As can be seen in Fig. 6, modified composites exhibited higher peak forces together with shorter contact times for all tested energies, suggesting a lower loss of transversal stiffness of these samples [19]. Subcritical impacts occurred at impact energies up to 0.5 J; the force curves

TABLE 4. Delamination threshold forces and critical energies of unmodified and modified pCBT-CF composites.

Sample	E_{crit} (J)	F_d (N)
pCBT-CF	0.33 ± 0.05	$1{,}562 \pm 71$
pCBT/EP 2.5%-CF	0.40 ± 0.14	$1{,}772 \pm 142$
pCBT/PMDI 1%-CF	0.48 ± 0.10	$2{,}199 \pm 100$

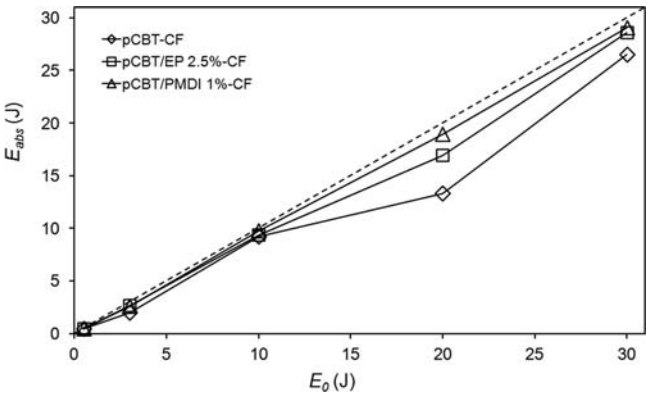

FIG. 7. Energy profile diagrams of pCBT-CF, pCBT/EP 2.5%-CF, and pCBT/PMDI 1%-CF composites.

in Fig. 6a are smooth and bell-shaped where no peaks are observed and no visible damage could be seen on the sample surfaces after impact. It is noteworthy that the absorbed energy of pristine pCBT-CF was relatively higher at subcritical impacts. Conversely at supercritical impacts, the absorbed energies of the modified samples were relatively higher, indicating a greater amount of plastic deformation.

At an impact energy of 3 J, the first damages in form of small indentations on the impacted surfaces were found, as is apparent from the load oscillations below the peak maxima of the force curves in Fig. 6b. Nevertheless, no damage at the back sides of the specimens was found. At this low energy level, the damage mode was local plastic deformation of the matrix. The damage mode at impact energies higher than 3 J was essentially the same for all samples; namely, horizontal and vertical cracks oriented parallel to the (0°/90°) fiber orientations on the impacted surfaces and localized fiber breakage at the impact points on the back surfaces. Crack lengths increased with impact energy. Nevertheless, the modified samples exhibited a more prominent distortion at the back surface which had a hemispherical shape with a diameter similar to the inner diameter of the annular support. This suggests that EP- and PMDI-modified pCBT possessed a greater ability to undergo plastic deformation whereas neat pCBT-CF showed little plastic deformation due to its brittle behavior, suggesting a greater overall damage.

Critical energy and delamination threshold force were fairly constant in the studied impact energy range (c.f. Table 3) and therefore may be considered as independent of the nominal impact energy [23]. The delamination threshold forces and related critical energies were averaged for all impact energies and results are presented in Table 4. The found delamination threshold force of T4 pCBT-CF was $1{,}562 \pm 71$ N, somewhat lower than the one reported by Agirregomezkorta and co-workers [19] (namely $1{,}760 \pm 35$ N). The results suggest that the modified composites exhibited a relatively higher delamination threshold. E_{crit} increased by 21 and 45% and F_d increased

by 13 and 41% for the EP- and PMDI-modified composites, respectively. Yeung and Broutman [24] showed that there is a correlation between the interlaminar shear strength and the absorbed impact energy of fiber-reinforced composites. The authors reported that the fracture initiation energy increased with increasing ILSS. Likewise, relatively higher critical energies can be seen for the modified composites in Table 4. Moreover, the authors found that the propagation energy and hence the total energy showed a minimum at a critical ILSS value. Above this critical value, the impact energy increased with ILSS and it was observed that the predominant fracture mode was fiber fracture. A similar tendency can be found in modified samples (see Tables 2 and 3).

The relation between impact energy and absorbed energy can be seen in the energy profile diagrams of the
F7 composites in Fig. 7. They show that the three composites behaved similarly for low impact energies up to 10 J. For higher impact energies, EP- and PMDI-modified composites absorbed more energy because they underwent a greater amount of matrix plastic deformation during impact, which was ascribed to the higher toughness of the matrix materials. Due to this greater deformability, a higher penetration threshold was deduced for the modified composites.

CONCLUSIONS

CBT was chemically modified with small amounts of chain extenders; namely, bifunctional epoxy resin and bi- or polyfunctional isocyanates. It was found that the chemical modifications did not significantly alter the physical and thermal properties or the morphology of the composites. On the other hand, interlaminar shear strength, flexural strength and failure strain of the chemically modified composites were considerably enhanced. Nevertheless, the flexural moduli slightly decreased due to the toughening effect of the chain extenders on the pCBT matrix. Low energy impact tests revealed that the modified composites absorbed relatively more energy as compared to unmodified pCBT composites. Moreover, critical energy and delamination threshold force were higher for modified composites. It can be concluded that toughening of pCBT with epoxy or isocyanates, namely PMDI and HDI, is very effective for improving the mechanical properties, most importantly the toughness of fiber reinforced pCBT composites.

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